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EFFECT OF TEMPERATURE ON THE INFRARED RADIATION PROPERTIES OF METHANE

by

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Abstract

In large scale fires, radiation feedback from the flame to the fuel surface can be an important factor determining the rate of fuel volatilization and the rate of flame spread. The radiant flux can be significantly attenuated by core gases that have absorption features in the infrared. Computer simulations that model flame spread require gas absorption data to accurately predict the radiation feedback.

The spectral absorptivity of the υ_3 band (at approximately 3000 cm^{-1}) of methane was measured at elevated temperatures. The measurements were performed at higher spectral resolution (4 cm^{-1}) than previously available measurements. The spectral mean parameters of line strength and line shape were determined for the Elsasser narrow band radiation model.

The measurements were made using a FTIR spectrometer coupled to a gas cell that was maintained at a constant temperature in a furnace. The partial pressure of the methane was varied between 5 and 95% yielding optical pathlengths between 1 and 14 atm-cm. The total pressure was maintained at 1 atm. Measurements were made at temperatures between 296 and 900K. The effect of spectral resolution on the measurements and derived parameters was examined. Spectral resolutions between 4 and 32 cm^{-1} were used.

The spectral absorption measured as a function of optical path length showed departures from Beer's Law dependence. Integrated band intensities, line strengths, and line shapes as a function temperature were derived from the data. The higher resolution measurements (4 cm^{-1}) yield line strengths having a highly irregular spectral dependence corresponding to the irregularity of the spectral data. This is in contrast to prior low resolution results that yield a smooth bell shaped distribution for the line strength as a function of the wavenumber within a band.

Introduction

In large scale fires, heat feedback from the flame to the fuel surface is dominated by radiation and is therefore the primary mechanism specifying fuel burning rates. Heat feedback to the fuel surface helps to volatilize the fuel which forms a cool, hydrocarbon-rich core between the flame and the fuel surface. When these core gases react, heat is released, which becomes part of a perpetuating cycle that sustains the flame and controls the heat flux and rate of spread. The core gases are an important part of the heat transfer process in that they absorb radiant energy from the flame. Therefore if accurate predictions of flame spread rates are to be made, the radiative properties of these gases must be known over a wide range of thermodynamic conditions.

Methane is a common hydrocarbon specie found in combustion environments, and is the focus of this work. It has three primary regions of absorption in the infrared: the υ_3 fundamental centered at approximately 3020 cm^{-1}, the υ_4 fundamental centered at 1306 cm^{-1}, and the $\upsilon_1+\upsilon_4$ combination centered at approximately 4220 cm^{-1}. As the temperature increases, the υ_3 and υ_4 fundamentals become the most significant absorption regions (Lee and Happel, 1964), while several other weak bands begin to appear.

Methane is commonly found not only in combustion environments but is important in atmospheric studies as well. It has therefore received a considerable amount of attention concerning its spectral nature. Varanasi (1971) investigated the line structure of the υ_3 band under high resolution (0.1-0.5 cm^{-1}) to identify individual line shapes and positions at room temperature under self-broadening conditions in addition to broadening by He, H_2, N_2, O_2, and air. His results revealed that collision-broadened lines in the υ_3 fundamental can be accurately represented by a Lorentz profile. Finkman et. al. (1967) calculated the integrated band intensity of the υ_3 fundamental using low resolution spectral transmittance data and the Goody statistical narrow band model. Lee and Happel (1964) presented correlations for total band absorption in several important IR bands as functions of temperature and optical density based on low resolution spectral absorptivity measurements. Brosmer and Tien (1985) applied the Elsasser narrow band model to their low resolution spectral absorptivity measurements and presented correlations for the υ_3 and υ_4 fundamentals. Brosmer and Tien (1987) studied horizontal PMMA pool fires by dividing the fire into two zones: a hot reaction zone and a cool fuel-rich core. In their analysis of the fuel core, which assumes a uniform temperature of 900 K and gray gas properties, they estimated that this region is responsible for attenuating 25-35% of the incident radiant flux.

Grosshandler (1993) presented a narrow band model (RADCAL) which predicts the spectral intensity and transmittance along a nonhomogeneous line of sight, based on both modeled and tabulated spectral absorption data for several gases commonly found in combustion environments. The parameters for methane that are currently used in RADCAL are based on low resolution data. The aim of the present analysis is to investigate the effect of instrument resolution and gas temperature on the measured and correlated spectral parameters of the υ_3 fundamental based on absorptivity measurements taken over a wide range of optical densities. In addition, an attempt is made to correlate the high resolution data in terms of the Elsasser narrow band model based on the analysis of Brosmer and Tien (1985).

Experimental Apparatus and Measurements

In the present study, the spectral absorptivity of methane was measured at various temperatures and optical densities using a Nicolet model 550 FTIR spectrometer coupled to an external gas cell that was enclosed in a furnace. Figure 1 shows the experimental setup. The gas cell was constructed of stainless steel tubing. BaF_2 windows placed on each end defined a fixed optical pathlength of 23 cm. The methane was diluted with nitrogen so that different concentrations could be examined while the total pressure was maintained at approximately 1 atm. The gases were mixed inside a manifold and flowed through the cell at a constant rate; the relative concentration of each gas was maintained by a series of rotameters located in the manifold upstream of the cell. Two rotameters were used to control the methane stream so that the concentration could be varied between 0.05 and 0.95 atm, providing a range of pressure-pathlengths between 1 and 14 atm-cm. The temperature of the gas mixture was monitored by placing thermocouples in the stream at the inlet and outlet of the cell to ensure that a uniform profile was maintained along the optical path. Measurements were made at temperatures of 296, 600 and 900 K and spectral resolutions of 4 cm^{-1} and 32 cm^{-1}.

The thermocouple uncertainty was +/- 2.2 K and the two temperature readings were generally maintained within this range. The main cause of temperature variation from the nominal value was uneven heating in the furnace. This effect was minimized through the use of a radiation shield and by controlling the total gas flow rate. C.P. grade methane, which specifies a purity of 99.1%, and prepurified grade nitrogen, which specifies a purity of 99.998%, were used.

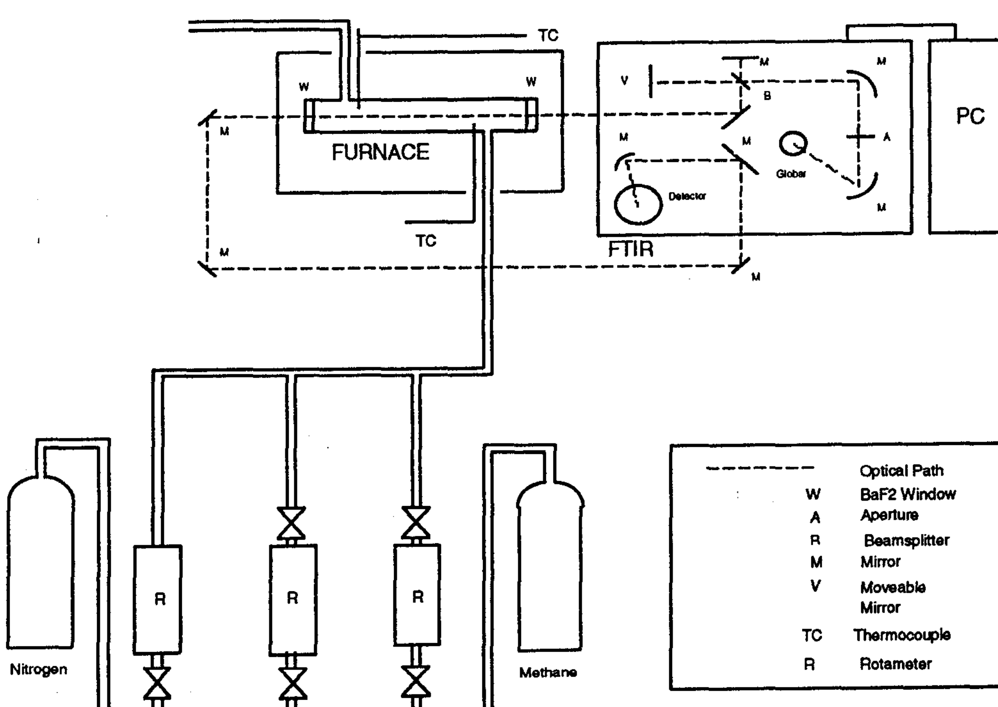

Figure 1 Experimental Configuration

Experimental Analysis

Figure 2 shows the effect of instrument resolution on spectral absorptivity. The absorption of the i^{th} band, A_i, defined as the area under each curve can be used as a measure of the net energy absorbed by the gas. The difference in resolution between 4 cm^{-1} and 32 cm^{-1} does not effect this value. If one is interested only in calculating total gas parameters then the low resolution measurements are adequate, and may be preferable from a computational standpoint. In combustion situations, however, more than one participating specie is typically present, and detailed spectral data is necessary to account for the regions where absorption bands from different gases overlap. For this reason, data collected at higher resolutions is desirable for the narrow band model correlations.

Narrow band radiation models correlate spectral data in terms of two band average parameters: the line strength (S_ω/δ_ω) and line shape $(\gamma_\omega/\delta_\omega)$, where S_ω is defined as the line intensity, γ_ω is the line half-width and δ_ω is the line spacing. Previous researchers (Lee and Happel, 1964; Brosmer and Tien, 1985) have determined that the υ_3 fundamental is best correlated by the Elsasser model, which assumes a uniform spacing, intensity, and width of individual lines within each absorption band, and assumes the lines can be represented by a collision-broadened contour. Figure 2 shows the υ_3 band centered at approximately 3020 cm^{-1}, in addition to two weak bands that overlap the P-branch. Examining the high resolution data, with the exception of the somewhat varying line intensity, the spectral characteristics of the υ_3 band are well approximated by the assumptions of the Elsasser model, and it was found to adequately correlate the present results.

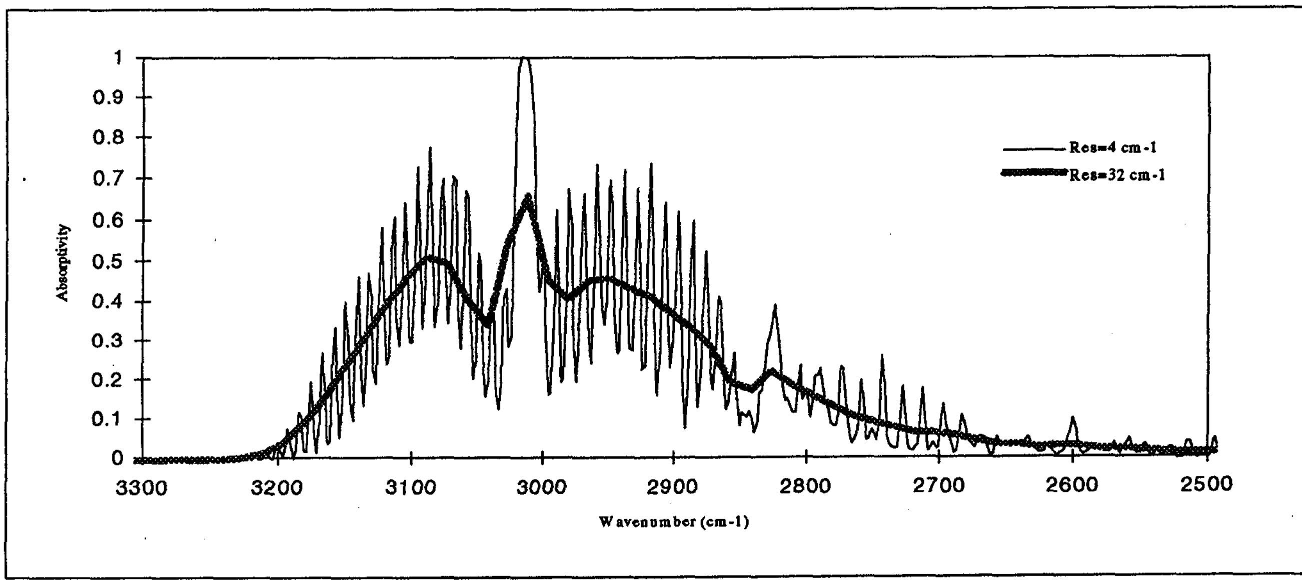

Figure 2 Spectral Absorptivity at T=296 K, X=5.72 atm-cm.

Brosmer and Tien (1985) have shown that for the Elsasser model, the line strength parameter can be expressed as:

$$S_\omega/\delta_\omega = \frac{\left(erf^{-1} a_\omega\right)^2}{2\pi X\left(\gamma_\omega/\delta_\omega\right)}\left\{1+\left[1+\left(\frac{\gamma_\omega}{\delta_\omega}\right)^2 \frac{16\pi}{\left(erf^{-1} A_\omega\right)^2}\right]^{1/2}\right\} \tag{1}$$

where a_ω is the experimentally determined spectral absorptivity and X is the optical density.

The integrated band intensity, α, is defined as the spectral integral of the line strength parameter:

$$\alpha(T) = \int_\omega S_\omega/\delta_\omega \; d\omega \tag{2}$$

At temperatures other than the reference state a correction is used:

$$\alpha(T) = \alpha_0 T_0 / T \tag{3}$$

The integrated intensity must be known before the band parameters can be derived. Once the intensity is known, the line shape parameter is determined iteratively through eqns. (1) and (2). The integrated intensity has been measured experimentally in previous studies (Finkman et. al., 1967), and is in fact independent of any band model. One method of determining the band intensity is to integrate the "apparent" spectral absorption coefficient:

$$\alpha = \lim_{X \to 0} \int_\omega \frac{-\ln(T_\omega)}{X} d\omega \tag{4}$$

in the limit as the optical density, X, approaches zero. Using this method with the present data a value of approximately 350 atm^{-1} cm^{-2} was derived, which falls within the range of values presented in a review by Brosmer and Tien (1985). In this analysis a value of 290 atm^{-1} cm^{-2} at STP was assumed based on its use in the development of RADCAL.

The line shape parameter was assumed to be of the form:

$$\frac{\gamma}{\delta} = \left(\frac{\gamma}{\delta}\right)_0 \left(\frac{P_{e_0}}{P_e}\right)^a \left(\frac{T}{296}\right)^b \tag{5}$$

where $P_e = (1 + 0.3\, P_m)$ is the effective pressure and P_m refers to the partial pressure of methane. The subscript $_0$ denotes the reference state at which P_m=0.25 atm and T=296 K. The line shape parameter at the reference state was determined to be 0.0256, and values of 1.9 and 1.48 were found from the experimental data to fit the constants a and b, respectively.

Results and Discussion

It was shown above how instrument resolution can effect the measured spectral absorptivity. In addition to affecting measured parameters, the resolution of the data plays a significant role in the narrow band model parameters. Figure 3 shows the line strength parameter calculated from data taken at a resolution of 4 cm^{-1} and compares it with the same parameter as it is currently used in RADCAL, which was calculated from data at a resolution of approximately 150 cm^{-1}.

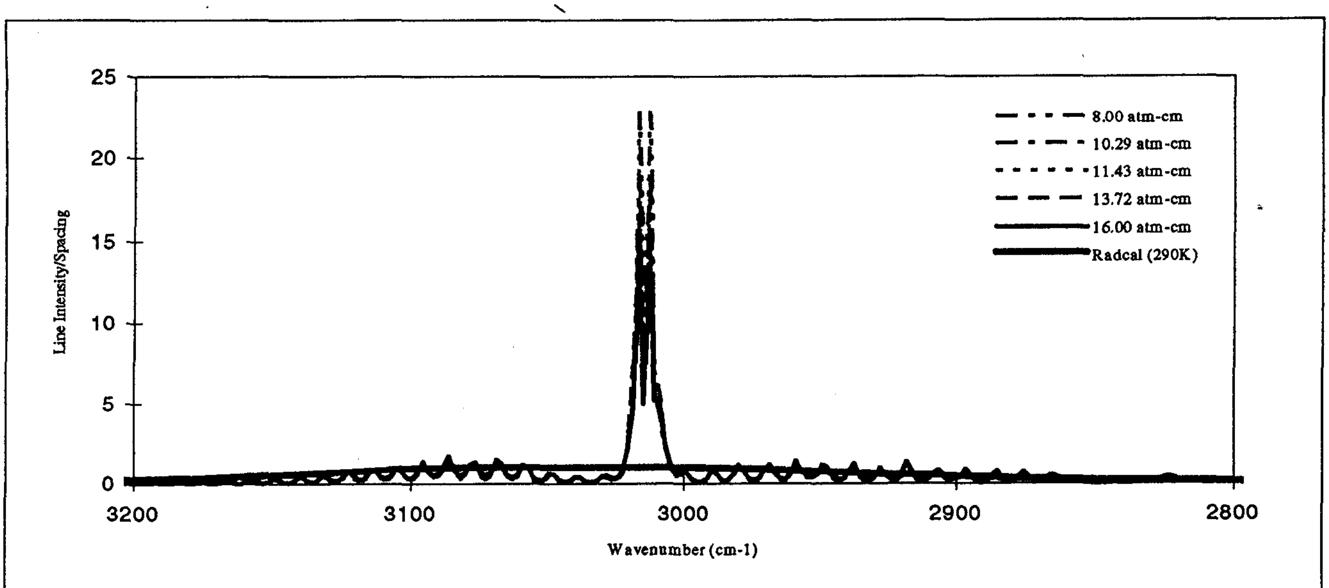

Figure 3 Comparison of the Spectral Line Strength Parameter at T=296 K

This figure demonstrates the applicability of the Elsasser model to the υ_3 fundamental by the manner with which the lines coincide over a wide range in optical densities. This result was to be expected by examining eqn. (1), where the optical density is normalized out of the expression for (s_ω/δ_ω). As was the case with the band absorption A_i, spectral resolution does not affect the integrated band intensity. Spectral resolution differences lie in the spectral variation of the line strength parameter. The highly resolved spectral features become especially significant in nonhomogeneous environments where considerable overlapping between bands of different gases can occur.

In the narrow band model the line strength parameter is analogous to the spectral absorption coefficient and is therefore the most significant parameter (DeRis, 1979). By normalizing the line strength parameter by the optical density, (s_ω/δ_ω) becomes solely a function of temperature. Figure 4 shows the inverse temperature dependence of (s_ω/δ_ω) over the range 2900-2950 cm^{-1}. In contrast, the temperature dependence of the spectral absorptivity is such that the band absorption, $A_i = \int_\omega a_\omega \, d\omega$, increases with temperature. Figure 5 shows the R-branch of the υ_3 band extending to shorter wavelengths with increasing temperature. The band absorption for the υ_3 fundamental at a resolution of 4 cm^{-1} and optical density of 8 atm-cm is given in Table 1. This data is in good agreement with the results of Lee and Happel (1964).

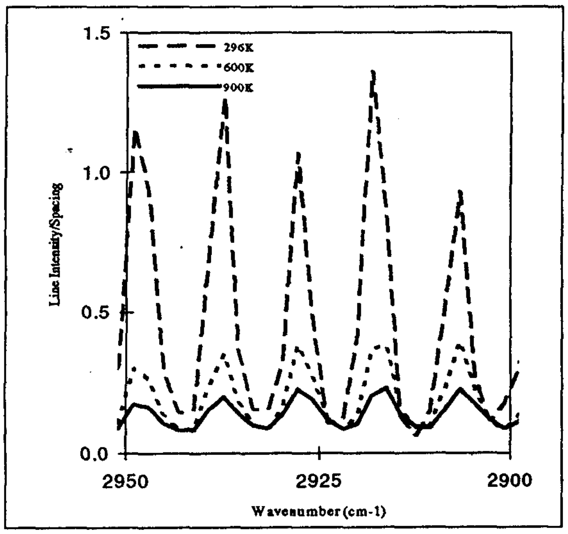

Figure 4 Line Strength Parameter at a Resolution of 4 cm^{-1} and X=5.72 atm-cm

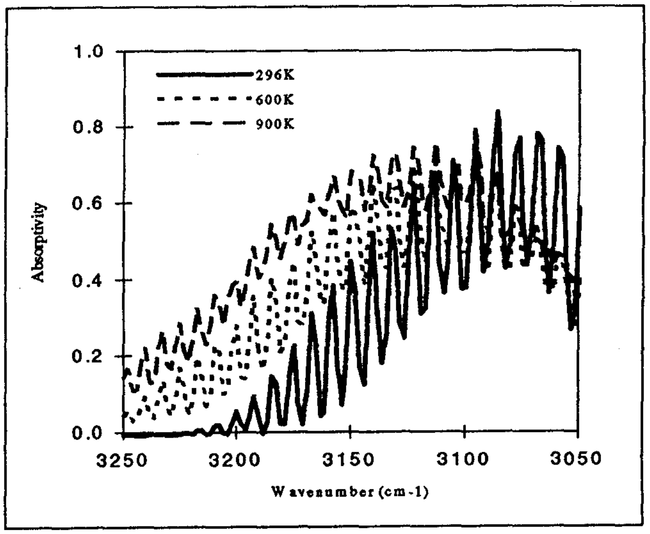

Figure 5 Spectral Absorptivity at a Resolution of 4 cm-1 and X=8.0 atm-cm.

Further evidence of the applicability of the Elsasser model to the spectral characteristics of the υ_3 fundamental is given in Fig. 6. In this figure the integrated intensity was calculated from spectral absorptivity data with eqns. (1) and (5). The horizontal lines represent theoretical values based on the measured value of α (290 atm^{-1} cm^{-2}) and the temperature dependence, eqn. (3). The advantage of representing the spectral data in terms of the narrow band model is that data collected at any temperature and partial pressure can be correlated with two expressions. Only one set of spectral data is required for each temperature once the correlations are known. However, one disadvantage is that each correlation is valid at a single resolution.

	Band Absorption A (cm^{-1})	Band Absorption A (cm^{-1})
Temperature (K)	Present Study X = 8.0 atm - cm	Lee and Happel X = 7.72 atm - cm
296	177.3	193.2
569		192.3
600	205.6	
668		214.0
873		242.3
900	254.0	
974		265.0

Table 1 Comparison between current band absorption data and the results of Lee and Happel (1964).

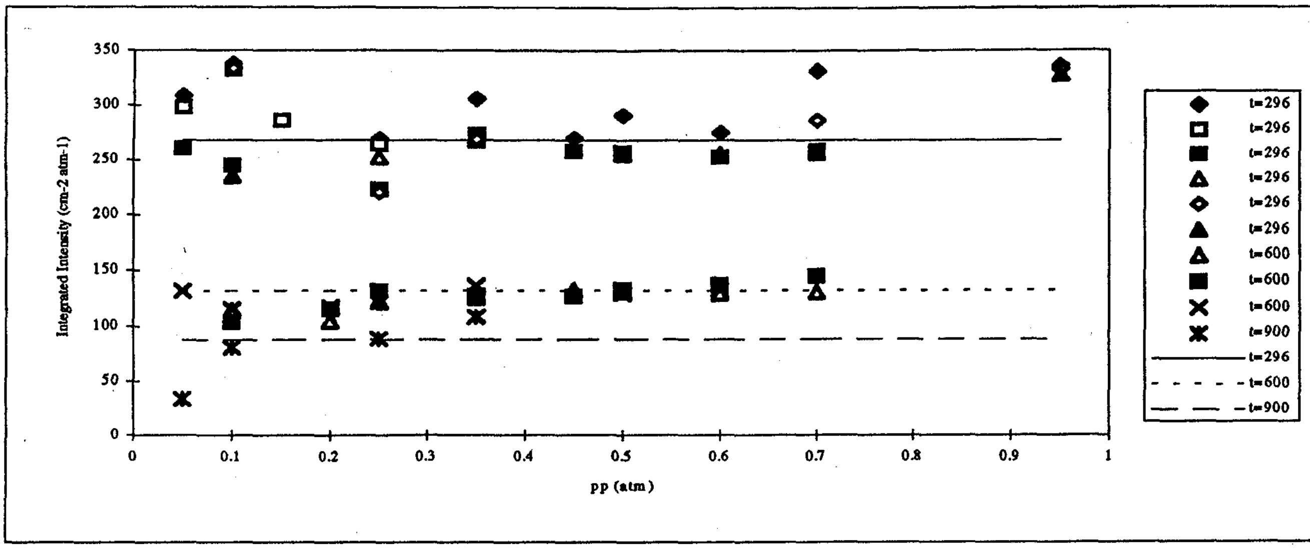

Figure 6 Comparison of Experimental and Theoretical Values of α for the υ_3 Band at T=296K, 600K, and 900K

Concluding Remarks

This analysis has demonstrated the benefits of using data collected at high resolution in situations where the spectral features of methane are important. While total band parameters are not affected by the resolution of the data, the measurement of spectral parameters is significantly affected by instrument resolution. Figures (2)-(4) show that the spectral absorptivity and line strength parameter at a resolution of 4 cm^{-1} can change by a factor of 2-5 over a spectral range of only 5 cm^{-1} while the variation at lower resolutions are much slower. This is important when the effects of band overlap between multiple gases must be accounted for. Due to the high temperatures found in combustion environments, the thermal dependence and range of applicability of spectral gas parameters are important factors. It has been shown here that the application of the Elsasser model to the infrared spectra of methane is valid for temperatures which are typical in the fuel-rich core region above the fuel surface in large pool fires. The validity of the data is demonstrated by the agreement shown with previous studies for both the integrated band intensity and band absorption.

List of Symbols

$a_\omega = 1 - T_\omega$	Absorptivity
$T_\omega = I/I_o$	Transmittance
$X = P_m L$ (atm-cm)	Optical Density

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